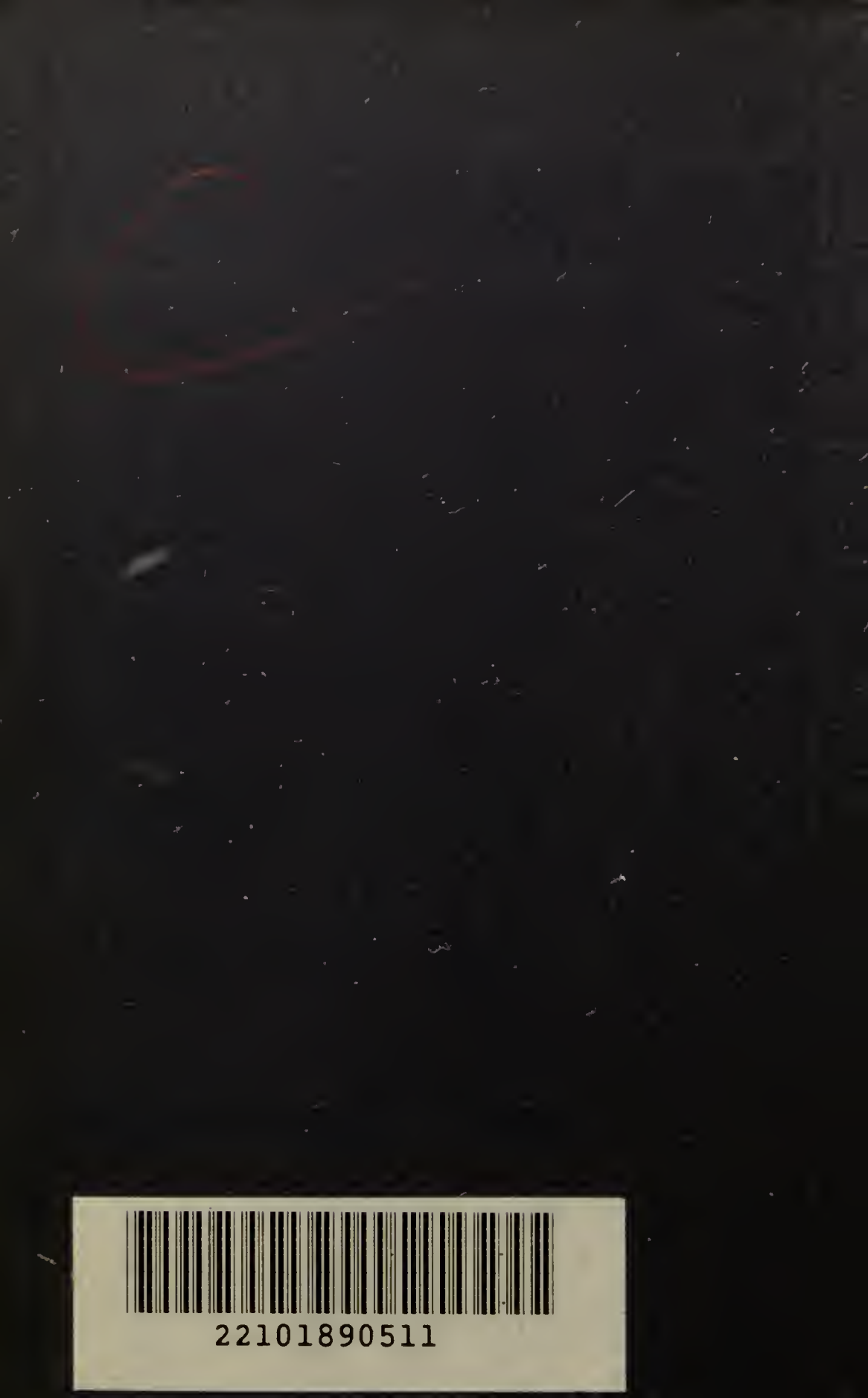
ANALYSIS OF POTABLE SPIRITS

S. A. VASEY


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GUIDE TO THE ANALYSIS OF POTABLE SPIRITS

GUIDE TO THE ANALYSIS

OF

POTABLE SPIRITS

SUPPLIED

BY

S. ARCHIBALD VASEY, F.I.C., F.C.S.

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PREFACE

THE object of the present work is to induce analysts to take up a more detailed examination of potable spirits than has hitherto been their practice, and to bring analytical methods to bear more minutely upon this question, in order that further light may be thrown on the extent of substitution which is going on in connection with the sale of spirits. The Sale of Food and Drugs Act ought to protect the purchaser of spirits in the same way as it protects the purchaser of foods, who is entitled to be supplied with an article of the nature, substance, and quality demanded; and for the purposes of the Act the expression "food" includes every article used for food or drink by man other than drugs or water. The author believes that the methods described in the following pages will, with a little practice, enable the analyst to declare whether a given spirit submitted to him is or is not genuine according to its description. Certain of the processes recounted are based upon those employed in

the Municipal Laboratory of Paris, and the author is indebted to Messrs. Masson et Cie., of Paris, for permission to use some of the descriptive matter and statistics contained in MM. Girard and Cuniasse's "Manuel Pratique de l'Analyse des Alcohols et des Spiritueux," published by them. To his colleague and friend, Dr. H. P. Cholmeley, the author owes considerable assistance in the translation of some of the technical sections of this work. The methods which have been introduced by analysts in this country, notably Allen, Hewitt, and Schidrowitz, have been embodied. The names of the authors and the references to original papers of the processes referred to are acknowledged in the text. The author has recorded his own experiences of the processes as applied to the discrimination of spirits, and has given what he has found to be in practice the procedure which in his hands has yielded concordant and trustworthy results. During a visit to Cognac recently he had the advantage of making the acquaintance of M. Ordonneau, whose classical inquiries on alcohol and spirits are well known, and the author takes this opportunity of expressing his thanks to M. Ordonneau for the valuable information which he gained while in his laboratory. As far as the author is aware, there is no treatise in

English that is exclusively devoted to the subject, and in most manuals on the analysis of foods and drugs, including malt liquors, wines, and spirits, the question of differentiating one kind of spirit from another is either ignored entirely or receives such scant treatment as to afford no practical guidance whatever. In endeavouring to fill this breach, the author would urge upon public analysts to give greater practical study than heretofore to this interesting and important branch of analytical work. The question is bound to occupy their attention sooner or later in connection with their official duties. Already several convictions have been obtained throughout the country under the Sale of Food and Drugs Act, in which the evidence of analysis was accepted as proving certain samples of "brandy" to be not genuine grape spirit.

S. ARCHIBALD VASEY.

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CONTENTS

CHAPTER		PAGE
I.	INTRODUCTORY - - - - -	11
II.	THE CHEMICAL CHARACTERISTICS OF POTABLE SPIRITS - - - - -	15
III.	METHODS OF ANALYSIS: STANDARDS, AND THE USE OF PURE ALCOHOL IN ANALYSIS; DISTILLATION OF THE SPIRIT FOR ANALYSIS	21
IV.	THE ESTIMATION OF ALDEHYDES AND ACIDS -	28
V.	THE ESTIMATION OF THE HIGHER ALCOHOLS -	36
VI.	THE ESTIMATION OF COMPOUND ETHERS -	57
VII.	THE ESTIMATION OF FURFURAL - -	60
VIII.	THE IMPORTANCE OF TASTE - - -	67
IX.	GENERAL CONSIDERATIONS OF THE RESULTS OF ANALYSIS - - - - -	71
X.	COLORIMETERS - - - - -	79
	APPENDIX: TABLES GIVING TYPES OF GRAIN AND ROOT SPIRITS, GENUINE WHISKIES, BRANDIES, RUM AND GIN, BLENDED SPIRITS	82



CHAPTER I

INTRODUCTORY

THE analysis of spirits has been much neglected in this country, partly because little attempt has been made to draw up a systematic scheme for their examination, but more particularly because no further control over the sale of ardent spirits has been exercised beyond that which relates to their alcoholic strength.

It is quite obvious that under such a régime it matters little whether a given spirit be called brandy, whisky, rum, or gin; the public analyst would record any single member of the series as genuine so long as it conformed to a certain alcoholic strength. This is not satisfactory, nor is it in the public interest, when we consider that, properly speaking, brandy should be the produce of distilled wine, whisky of malt, and rum of sugar, and so on, each spirit possessing its own special characteristics.

It should not be difficult, therefore, one would think, to define each spirit with regard to its origin; and the impression of the public is that, when brandy is asked for, grape spirit is supplied, while whisky is generally understood to be a spirit obtained from barley malt, and rum a spirit distilled from cane-sugar or molasses. The fact that the strictly genuine article is rarely supplied, except it be very specially requested, is due to the existence of much cheaper sources of alcohol than are grapes, malt, or cane-sugar, and to much more economical methods of producing it. Alcohol can be obtained from almost anything nowadays, even refuse of all kinds, and the patent still would seem to be capable of purifying it sufficiently to make it drinkable and suitable for blending purposes. The introduction of grain or neutral spirit was never demanded by the public taste: it was dictated solely and simply by economical motives. The time required for maturing genuine whisky is thus saved, and the practice of blending is carried to an enormous, if not appalling, extent, with handsome profits to the blenders. There is no control over the character or purity of the grain spirit used for this purpose; it may be made from any loathsome material, so long as it is capable of alcoholic fermentation. Clearly the

public interest and health need guarding here, and there is every reason why that clause of the Food and Drugs Act providing that an article should be of the nature, quality, and substance demanded by the purchaser should be enforced in the case of the sale of spirits. It is a serious thing that when brandy—*i.e.*, genuine grape spirit—is demanded, a much inferior spirit is supplied—pure grain spirit, perhaps, flavoured with French plums, "oil of Cognac," or even a little rum—possessing none of the medicinal qualities of genuine brandy.

Attempts have already been made to amend the law relating to the sale of spirits, and recently a Bill was presented by Sir Herbert Maxwell to Parliament, providing for the marking of casks and other vessels containing whisky. The memorandum of the Bill is as follows :

"The object of this Bill is to secure to purchasers of whisky a clear statement whether it is a whisky made from barley malt alone, or is in part a spirit made from unmalted grain. To carry out this object, the Bill proposes to enact that all whisky shall, from the time of leaving the distillery till sold to the consumer, be described by a mark or label on the cask or bottle as 'malt whisky,' or 'grain whisky,' as the case may be. Provision is made for

similar information being given to persons purchasing whisky on draught.

"Under the existing law the Inland Revenue authorities are furnished with returns of the materials used in each distillation, and they have, by means of the permits or certificates required on the removal of spirits, and the stock-books required to be kept by rectifiers, dealers, and retailers, the information necessary for tracing the whisky till it reaches the retailer. Power to prosecute for offences against the Bill is therefore given to officers of Inland Revenue, but *persons authorized by local authorities having the execution of the laws relating to food and drugs are also to have power to prosecute*, and to be supplied by the Inland Revenue with the information necessary for that purpose." (The italics are the author's.)

CHAPTER II

THE CHEMICAL CHARACTERISTICS OF POTABLE SPIRITS

THE patent or fractionating still is practically the key to the situation as regards the analysis of potable spirits. As is well known to chemists and distillers, this ingenious apparatus produces a very strong and practically featureless, because pure, spirit. It separates certain by-products of fermentation during the distillation process, with the result that when the spirit is highly rectified it is very pure and free from characteristic odour and flavour. The simplest form of still, or the pot-still, which is used in the production of brandy, whisky, and rum, yields, on the other hand, a more or less impure spirit, owing partly to the formation of secondary products of fermentation, and partly because of bodies formed during distillation, which, coming over with the spirit, impart to it a flavour and odour characteristic of the material used in the fermentation.

It is only in the pot-still spirit that these products occur to any extent; they are nearly, if not entirely, eliminated in patent spirit, according to the degree of rectification. It is thus necessary that pot-still spirits should be matured by age, while with patent spirit no such maturing process is called for, unless, owing to partial rectification, there is a small percentage of by-products present. The use of patent spirit, therefore, obviates to a large extent the expense of storage, which is necessary for mellowing the raw spirit of the pot-still to render it, not only drinkable, but palatable and of agreeable flavour. Flavour is essential to potable spirits, and patent spirit, on account of its tastelessness, must be flavoured, which is generally accomplished by adding a small proportion of old, well-matured pot-still spirit to it. Foreign flavourings can also doubtless be used, and there is much brandy on the market which is absolutely destitute of grape spirit, just as there is much whisky that is absolutely destitute of malt spirit.

It would be superfluous, of course, to use barley malt or grape juice for the fermentation when the separation of the spirit is consigned to the patent still. To begin with, these materials are much more expensive sources of alcohol than are potato starch,

maize, beetroot; and, secondly, the flavours characteristic of the grape or barley malt would be to a great extent lost in the patent still, and, in fact, the product would resemble patent spirit produced from grain or root. Plain rectified spirit is no doubt made in France and elsewhere from unsound wines, or wines that would not make good brandy, the patent still being used to eliminate undesirable by-products.

It is evident that pot-still spirit cannot be dispensed with so long as flavour is looked for of the kind which has characterized brandy and whisky from the earliest time they were made. Pot-still spirit, whether brandy or whisky, is the agent which the blender adds to featureless spirit in order to give it a characteristic flavour—the genuine flavour of grape or malt spirit, as the case may be. To some extent, just as grain or patent spirit is poor as regards flavouring matters, so is it nearly, if not entirely, free from substances other than alcohol—from the chemical point of view it is, in fact, a much purer spirit than pot-still spirit. On the other hand, pot-still spirit is more or less strongly flavoured according to the material used, and chemical analysis would seem to indicate that flavour is coincident with the presence of secondary products

arising from interaction, fermentation, or distillation, amongst which may be reckoned compound ethers, volatile acids, aldehydes (including furfural), and alcohols of the higher series—*e.g.*, amylic and butylic alcohol.

There is little doubt that the secondary or by-products of a pot-still spirit comprise other products not present in grain or patent spirit, but those just enumerated are, in the author's experience, sufficient to determine by chemical analysis whether a spirit conforms to the description given of it. The premises are, then, that a grain or patent spirit is free from, or contains a relatively small proportion of, by-products, or *impuretés*, as the French chemists call them, while a pot-still spirit—as, for example, brandy made from grapes, whisky from barley malt, rum from sugar or molasses—contains these *impuretés* in relatively large amounts, and in a varying ratio to each other, according to the origin of the spirit. It is thus not difficult to distinguish by means of chemical analysis pot-still spirit from patent spirit.

When a potable spirit is found to be chemically featureless, it indicates, as a rule, an all-grain spirit, or the presence of a large proportion of grain or patent spirit, and its flavour is feeble or "delicate"

when compared with a pot-still spirit or an all-malt or all-grape spirit. That being so, the results of a chemical analysis based upon an accurate determination of the secondary or by-products, or *impuretés*, gives a very fair indication of the nature of the spirit. To illustrate this (see also Tables VII., VIII., IX., X., XI.), some typical analyses made by the author are given in the following table. The results are given in grammes per 100 litres of absolute alcohol present.

TABLE I.

By-products.	*Patent Spirit intended for Whisky Blending.*	*Genuine Gin.*	*Genuine Pot-still Scotch Whisky Eight Years Old.*	*Sold as Scotch Whisky, but probably all German Patent Spirit.*	*Genuine Cognac Brandy Ten Years Old.*	*Genuine Rum.*	*Brandy mixed with Plain Spirit.*
Volatile acidity reckoned as acetic acid ..	8·40	nil	48·00	16·80	74·52	28·00	79·41
Aldehydes	4·90	1·78	14·20	10·00	16·56	8·40	7·35
Furfural	0·35	nil	4·00	nil	1·65	2·80	0·61
Ethers as ethyl acetate..	23·80	37·28	89·68	8·23	109·29	399·00	32·35
Higher alcohols	trace	44·60	200·00	nil	124·20	90·60	49·02
Total by-products ..	37·45	83·66	355·88	35·03	326·22	528·80	168·74

CHAPTER III

METHODS OF ANALYSIS

I. Standards, and the Use of Pure Alcohol in Analysis

Pure alcohol is a *sine quâ non* in the preparation of all standard solutions, and for the purpose of making up solutions to a definite volume. That is to say, the alcohol used in the colorimetric processes, as well as in the preparation of standard solutions, must be free from aldehyde, furfural, and higher alcohols. In the author's experience, rectified spirits of wine or methylated spirit "denatured" simply by wood spirit is better than absolute alcohol, and its use is certainly more economical. This will be found to be comparatively free from aldehydes, furfural, and higher alcohols, and to give negative reactions (which should be ascertained) with the colour reagents, while the ordinary absolute alcohol frequently contains aldehydes. Ethers, if present, may be removed by distillation

after saponification with potash, and aldehydes, including furfural, by means of Hewitt's reagent (*Journal of the Society of Chemical Industry*, January 31, 1902), the sodium salt of phenyl-hydrazine parasulphonic acid. MM. Girard and Cuniasse add to every litre of alcohol 3 or 4 grammes of chlorohydrate of metaphenylenediamine, or the same quantity of phosphate of aniline, leaving the mixture for some days, or just boiling it for an hour under a reflux condenser, and finally distilling off the alcohol slowly, rejecting the first few c.c., and stopping the process as soon as nine-tenths of the alcohol has passed to the receiver. It will be found that Hewitt's reagent, employed in the same way, answers admirably, and the addition of metaphenylenediamine is satisfactory when a distillate free from furfural is desired. The author, however, has found no difficulty in procuring rectified spirits of wine, which needs no preliminary purifying treatment on either of the lines indicated. An abundant stock of dilute alcohol (50 per cent. strength) should be available when colorimetric determinations are to be made.

In ordinary practice the author has found the following strengths of solutions for colorimetric analysis convenient: Aldehyde, 0·05 gramme per

litre; furfural, 0·01 gramme per litre; and iso-butylic alcohol, 2 grammes per litre. Stronger solutions in 50 per cent. spirit should be kept in stock, from which to make the dilute solutions. They should be kept in the dark in non-actinic glass bottles. A solution of aldehyde may be standardized by starting with ammonia aldehyde, as described in the chapter on Aldehydes. There is no difficulty in obtaining pure furfural or iso-butylic alcohol (or amyl alcohol) from dealers in fine chemicals—Messrs. Baird and Tatlock, for example, or Merck, of Darmstadt. The pure substances should be weighed in flasks containing alcohol.

In order to make the conditions of experiment as far as possible the same, the best plan is, after making up the standards with 50 per cent. alcohol, to put the solutions in the still, and treat them in the same way as the spirit under examination—*i.e.*, to distil off nine-tenths, and make up the distillate with water. Thus, 200 c.c. of standard furfural made up with pure spirit of 50 per cent. strength are distilled until there is 180 c.c. of distillate. The distillation is then stopped, and the distillate made up to 200 c.c. with water. The alcoholic strength will be 50 per cent. The standard so obtained

should be marked "distilled standard," and its strength as regards furfural may be taken to be the same as the standard before distilling. By this plan the spirit would be assayed under precisely the same conditions of experiment. Similar steps may be taken with the standard aldehyde and higher alcohol, though they may be considered to be superfluous. At any rate, such precautions would be excessive in the case of colourless spirits, which are at the same time free from extractive matters. Such, however, with, perhaps, the exception of unsweetened gin, hardly exist amongst potable spirits.

II. DISTILLATION OF THE SPIRIT FOR ANALYSIS

For colorimetric analysis the spirit must be distilled, in order to separate the volatile by-products from colouring matters and extractives. It would appear to be an advantage if in these colorimetric determinations the distillation of the spirit could be dispensed with. Hewitt and Schidrowitz have tried removing the colour with lead acetate, etc. (see p. 34), so that the spirit after filtration from the precipitated colouring matters can be submitted

directly to the colorimetric process. By adopting standards, however, distilled under the same conditions as the potable spirit under examination, any error arising from distillation is for all practical purposes eliminated. P. Schidrowitz (*Journal of the Society of Chemical Industry*, June 30, 1902) recommends a method of steam distillation for the separation of colouring and extractive matters. The distilling flask is provided with a cork covered with tinfoil, through which passes, to within a few millimetres of the bottom of the flask, a glass tube suitably bent and connected with a steam supply. First, roughly, nine-tenths of the liquid is distilled by means of a gas-burner in the ordinary way, and then steam is turned on, and the burner under the flask so regulated that the contents of the same are reduced to about 5 c.c. by the time 150 c.c. in all have passed over. The author does not find any advantage in this method over simple distillation. It is not necessary to carry the distillation much further than when alcohol ceases to come over, for it will be found that the ethers, higher alcohols, aldehydes, and furfural in the original spirit come over with the first runnings, which are of high alcoholic strength. This laboratory experience is in accord with that of the distillery. Further,

if the distillation be pushed too far, there is risk of furfural being formed in the experiment, and of other decompositions taking place.

Dr. Hewitt (*Journal of the Society of Chemical Industry*, January 31, 1902) states that, since distillation cannot be carried to dryness, on account of charring the residue, and furfural being of a high boiling-point—the boiling-point of furfural is 161° C. —all the furfural will not be obtained in the distillate by one distillation. He proposes, therefore, to distil rapidly "to nearly the last drop," then to add 10 c.c. of pure methylated spirit and distil again, and then another 10 c.c., and yet a third 10 c.c. In this way the residue in the flask will be found to yield no reaction for furfural. The author finds, however, that a solution containing 0·01 furfural per 100 c.c. of 50 per cent. alcohol yields the whole of the furfural in 40 c.c. of the distillate. The boiling-point of furfural, when it occurs in such small quantities as in spirits, does not affect its being carried over just as is the case with essential oils; a parallel case also is that of the higher alcohols, which will be found in the first fraction of the distillate, though their boiling-point is considerably higher, of course, than ethylic alcohol. The higher alcohols, as well as the ethers, will be

found to be in considerable excess in the first runnings of the pot-still in the distillation of both brandy and whisky. Furfural, it may be noted, is very readily formed on the mere distillation of a weak solution of saccharine matter. Thus, Schiff found that by distilling 0·00005 gramme of sugar, a distillate is obtained giving a marked furfural reaction.

In the writer's experience, rapid distillation until nine-tenths of the spirit has passed into the receiver is all that is required, and the results are accurate. The residue in the flask from the distillation of 200 c.c. of spirit may be reserved for the examination for extractives, sugar and tannin.

For the estimation of aldehydes, furfural, compound ethers, and higher alcohols, 200 c.c. of the spirit should be distilled until 180 c.c. are collected in the distillate. It should then be made up to 200 c.c. with pure distilled water at 15·5° C., and thoroughly mixed, and the specific gravity determined either by weighing a known volume or by means of the Westphal balance or hydrometer. The alcoholic strength may thus be incidentally determined. The distillate is then reserved for the determination of aldehydes, furfural, ethers, and higher alcohols, according to the methods described in the following chapters.

CHAPTER IV

ESTIMATION OF ALDEHYDES AND ACIDS

I. Aldehydes

Aldehydes exist probably for the most part in brandy, whisky, and rum as acetaldehyde CH_3COH, but there is also furfuraldehyde in small quantity present. The aldehydes in general have their origin in the oxidation of corresponding alcohols, while furfural is a product of the decomposition of carbohydrates. Pentoses are formed from woody fibre, and these, when heated with dilute mineral acid solution, give furfural. The proportion of aldehydes in potable spirit, however, of the CnH_2nO series is infinitely greater than that of furfural, and in the estimation of aldehydes by the colorimetric process about to be described the furfural may be disregarded. The reagent introduced by Guyon and Schiff (*Comptes Rendus de l'Académie des Sciences*, 1887, p. 1182) for the estimation of aldehydes is prepared in the following manner : A solution of fuchsine is prepared by

dissolving 1 gramme in a litre of water, and also a solution of bisulphite of soda of a strength corresponding to a specific gravity of 1360; 150 c.c. of the fuchsine solution and 100 c.c. of the bisulphite solution are added to a litre of pure distilled water, and finally 15 c.c. of pure sulphuric acid (66 per cent.) are added. The mixture is shaken, and after some hours it should be quite clear and colourless. Unless a great number of analyses are being conducted, it is advisable to keep the solutions separate, and to mix the quantity of each to make sufficient reagent just when required. Generally, it will be found convenient to take 5 or 10 c.c. of the spirit (50 per cent. alcohol) for the estimation, and to add 4 c.c. of bisulphite fuchsine reagent, and make up to 20 c.c. with 50 per cent. alcohol. In most cases (brandy and whisky) 5 c.c. of the spirit will suffice, made up to 20 c.c. with 50 per cent. alcohol. The standard-aldehyde is made up in one or other of the following ways. MM. Girard and Cuniasse direct that the aldehyde should be freshly prepared, for it must be remembered that this body polymerizes with great facility, and paraldehyde has not the same action upon the bisulphite reagent. Pure acetic aldehyde boils at 20·8° C., and has a density of 0·791 at 15° C. The standard solution may be made up by weight, or as

containing so many grammes of pure aldehyde per volume of alcohol of 50 per cent. strength. In the former case the following is an example given by MM. Girard and Cuniasse. If 1·922 grammes of aldehyde are taken to make a solution of 1 gramme per 100 c.c., the volume of the solution should be 192·2 c.c. The aldehyde occupies a volume of $\frac{1{\cdot}922}{0{\cdot}791} = 2{\cdot}40$ c.c. and 192·2 c.c. − 2·40 c.c. = 189·8 c.c. of alcohol to be added, or 177·3 grammes of alcohol at 50° (specific gravity 0·934). The solution, then, should weigh 177·3 grammes + 1·922 grammes = 179·22 grammes. The contents of the flask whose weight is known must be brought to 179·22 grammes with alcohol of 50 per cent. strength. The resulting solution would be a 1 per cent. by weight solution of aldehyde. In weighing out the aldehyde, it is best to drop it into the flask containing some alcohol from a pipette, so as to avoid loss in weighing. The solution of aldehyde in alcohol is permanent, but it is a good precaution to preserve the solution in a non-actinic glass bottle in a dark cupboard. MM. Girard and Cuniasse observe that the same procedure in regard to the preparation of a standard aldehyde solution may be followed in making up the other standard solutions. By adding alcohol of 50 per cent. strength to them, weak standard solu-

tions may be prepared according to requirement. The advantage of making weight for weight standard solutions is doubtful; it is preferable to have a given weight of substance dissolved in a known volume of alcohol at 50 per cent. strength, and it is convenient to record the results of analysis in grammes per hectolitre of alcohol, or, what is the same thing, in milligrammes per 100 c.c.

There must always be doubt as to the percentage of real aldehyde contained in the specimens supplied by the makers. The strength of a standard solution of aldehyde, however, may be insured by following the procedure adopted by M. Rocques, who takes pure ammonia aldehyde as the starting-point of the standard aldehyde solution. This substance may very readily be prepared in the pure state in the laboratory, but the commercial product answers the purpose quite well. Advantage is taken of the fact that aldehyde ammonia is soluble in alcohol, and is decomposed into a corresponding salt and aldehyde by dilute acid. The ammonia aldehyde is first ground in a mortar with ether, and the ether decanted several times. After drying in a current of air and then in a vacuum over concentrated sulphuric acid, 1·386 grammes of the ammonia aldehyde are weighed out. This quantity corresponds to

1 gramme of aldehyde. The salt is perfectly definite, having the formula $CH_3CHOHNH_3$. The salt is placed in a small flask graduated to 100 c.c., and dissolved in 50 c.c. of alcohol of 96 per cent. strength. To this are added 22·7 c.c. of normal alcoholic sulphuric acid, which throws out ammonium sulphate. The volume is made up to the 100 c.c. mark with alcohol of 96 per cent. strength and an addition of 0·8 c.c. of alcohol, to compensate for the volume of the ammonium sulphate. The mixture is shaken and allowed to stand for twenty-four hours, and then filtered. It represents an alcoholic solution of aldehyde containing 1 per cent., which can be diluted to the strength convenient for the estimation (viz., 0·05 or 0·10 gramme of aldehyde per litre of alcohol at 50 per cent. strength). Solutions of aldehyde made directly from aldehyde may be standardized by means of this solution.

In general, 5 c.c. to 10 c.c. of the distillate of a potable spirit of 50 per cent. alcoholic strength is sufficient for the estimation of aldehyde. To this quantity in a graduated cylinder is added 4 c.c. of bisulphite of fuchsine solution, and the whole made up to the 20 c.c. mark. Five c.c. of the standard solution are treated in the same way, and the two cylinders are left in the cold for twenty minutes,

when the tints are compared. The maximum intensity is developed in this time. By matching the two solutions, the amount of aldehyde in the spirit under examination may be determined. This can be done by decanting one or other of the coloured fluids until the columns are the same tint and noting the relative volumes. (See chapter on Colorimeters.)

P. Schidrowitz states that the estimation of the aldehydes in whisky by the above process has one serious drawback (*Journal of the Society of Chemical Industry*, June 30, 1902), which is that when the distilled liquid is treated with the reagent an opalescence or turbidity is produced which renders the colorimetric estimation difficult. The author has never encountered this drawback, which may possibly arise from employing too large a volume of distillate (5 c.c. is sufficient in general), or a distillate of a higher alcoholic strength than 50 per cent. However, Schidrowitz was led to modify the process after observing that when the reagent was added to an undistilled sample of a colourless whisky the liquid remained perfectly bright. He ultimately obtained satisfactory results by partially decolourizing the spirit (complete decolourization appears to be impossible by means of precipitants), and colouring

slightly the standard solution in imitation of the sample. The substance chosen for partially decolourizing the spirit was basic lead acetate, removing the excess by means of a saturated solution of potassium sulphate. Neither of these reagents influence the colour produced by the rosaniline reagent, as was shown by experiment. The control solution is coloured with either tincture of galls or the colouring matter derived from evaporating a genuine cask-coloured spirit to dryness on the water-bath, and taking up with pure 50 per cent. alcohol. Caramel is inadmissible for the purpose, as, unlike the other colourings suggested, it influences the colour reaction. This process has the decided advantage that any loss or change of aldehydes due to distillation is avoided.

II. VOLATILE AND FIXED ACIDITY.

The acidity, both volatile and fixed, is best determined separately by titrating a known volume of the original spirit (25 c.c.) with decinormal solution of baryta, which gives the total acidity. A further 25 c.c. is evaporated to dryness three or four times on the water-bath, and the residue taken up with water, and titrated as before with decinormal baryta, using in both cases phenolphthalein as

indicator. The number of c.c. used multiplied by the factor 0·0075 gives the fixed acidity in terms of tartaric acid in the amount taken. By deducting the number of c.c. of decinormal baryta solution used for the estimation of fixed acidity from the number used for the total acidity (*i.e.*, with the 25 c.c. before evaporation), a difference is obtained which, when multiplied by the factor 0·006, gives the volatile acidity as acetic acid. The determination of the fixed acidity is important, as some indication is thereby given as to whether or not the spirit has been stored in sherry-casks.

CHAPTER V

THE ESTIMATION OF THE HIGHER ALCOHOLS

The term "higher alcohols" is convenient, and includes, broadly, propyl alcohol, normal butyl alcohol, iso-butyl alcohol, and amyl alcohol. The so-called fusel oil contains these bodies in varying proportion, according to the nature of the spirit and the materials from which the spirit has been derived. MM. Clandon and Morin and Ordonneau give the following as the composition of fusel oil from brandy:

Percentage Composition of Fusel Oil according to Clandon and Morin and Ordonneau.

	Clandon and Morin.	*Ordonneau.*
Propyl alcohol	11·9	11·7
Normal butyl alcohol ..	49·3	63·8
Iso-butyl alcohol	4·5	0·0
Amyl alcohol	34·4	24·5

In the fusel oil of raw potato and grain spirit the proportion of amylic alcohol in general predominates, that of iso-butyl alcohol next, with

relatively small amounts of iso-propyl alcohol and traces of normal propyl and normal butyl alcohols. It is doubtful whether spirits are physiologically bad because of the proportion of "higher alcohols" or fusel oil which they contain. The amount seldom exceeds 0·3 per cent. Age would not appear to diminish this amount, though it is probable that the various higher alcohols undergo some not well-defined change. Very old brandy often contains three times as much higher alcohols than young brandy, and yet experience is in favour of the former being more wholesome than the latter. Several processes have been suggested for the determination of higher alcohols, some purely of an empirical kind, and others of an exact nature. To the former belong the colorimetric processes, which, however, give very useful and instructive indications, as we shall presently see; to the latter belong those processes based on the estimation of the corresponding acids produced by oxidizing the alcohols. It is probably due to Dupré that we now possess a satisfactory method for the determination of higher alcohols, and the first intelligible results as to the amount of "fusel oil" in brandy were published by him in 1879.

Dupré's process was improved by Marquardt, who extracted the diluted spirit with chloroform, sub-

sequently separating the chloroform and oxidizing the higher alcohols contained in it with chromic acid mixture. On distillation the acids were obtained, and boiled with an excess of carbonate of barium, the liquid filtered, evaporated, and the valerate of barium weighed.

A. H. Allen found several inconveniences and sources of error in working this process (*Journal of the Society of Chemical Industry*, April 30, 1891), and was led to try carbon tetrachloride in the place of chloroform for extracting the higher alcohols from the diluted spirit. As he points out, this solvent has the advantage of boiling at a higher temperature, and hence obviating the necessity of oxidizing under pressure, and is further obtainable in a state of such purity as to yield (contrary to chloroform) no mineral acid whatever on oxidation. The distillate, therefore, can be titrated with standard baryta water, and the amyl alcohol calculated from the valeric acid found, or the solution of valerate of barium can be evaporated and the salt weighed. Allen suggests certain precautions, as, for example, the addition of salt to the spirit, so as to secure complete extraction of the amyl alcohol. The following results referring to the amount of amylic alcohol in various whiskies were obtained by various authors :

TABLE II.—AMYLIC ALCOHOL IN WHISKY.

Observer.	*Date.*	*Description of Spirit.*	*Per 100 Parts of Proof Spirit.*	*Grains per Proof Gallon.*	*Grammes per 100 Litres of Absolute Alcohol.*
A. Dupré ..	1877	Scotch whisky	0·095	66·5	166·25
		Cape Smoke	0·120	84·0	210·00
		Common "Samsho"	0·090	63·0	157·50
		Fine "Samsho"	0·065	45·5	113·75
Sir C. Cameron	1880	Potheen	0·184	128·8	321·00
A. H. Allen ..	1890	Irish whisky—disputed sample	0·070	49·0	122·50
		Irish whisky—1 (Typical specimens)	0·077	53·9	134·75
		Irish whisky—2 (Typical specimens)	0·114	79·8	299·50
		Irish whisky—3 (Typical specimens) ..	0·061	42·7	106·75
		Irish whisky—4 (Typical specimens)	0·069	48·3	120·75
		Irish whisky—5 (Typical specimens)	0·078	54·6	136·50
		Irish whisky—6 (new)	0·087	60·9	152·25
		Irish whisky—7 (old)	0·080	56·0	130·00
		Scotch whisky—1 (new)	0·085	59·5	148·75
		Scotch whisky—2 (old)	0·080	56·0	130·00
		Scotch whisky—3 (new)	0·062	43·4	108·50
J. Bell ..	1890	Whisky A (new)	0·120	84·0	210·00
		,, ,, (old)	0·140	98·0	245·00
		Whisky B (new)	0·090	63·0	157·50
		,, ,, (old)	0·120	84·0	210·00
		Whisky C (new)	0·080	56·0	130·00
		,, ,, (old)	0·140	98·0	245·00
		Whisky D (new)	0·060	42·0	105·00
		,, ,, (old)	0·070	49·0	122·50
		Silent Spirit Native (new)	0·027	18·9	47·25
		,, ,, ,, (old)	0·027	18·9	47·25
		,, ,, Foreign (new)	0·009	6·3	15·75

Allen remarks that it cannot be too clearly understood that these results represent the apparent fusel oil without the separation of the ethers and other interfering bodies, and not the actual true amylic alcohol, which would be materially lower. He believes the results are gravely in excess of the truth, owing to the spirit not having been previously treated with alkali. P. Schidrowitz employs the following modification of this method, which in the author's hands has given consistent results : To 100 c.c., or preferably 200 c.c., of the spirit 0·15 to 0·2 gramme of caustic potash is added, and the whole boiled for an hour under the reflux condenser. The alkali saponifies both the ethers and the furfural. The contents of the flask are then transferred to the distilling flask, and the distillation carried on as described on p. 25. The distillate is diluted with concentrated brine until it has a specific gravity of about 1·10. It is then extracted with 40, 30, 20, and 10 c.c. respectively of carbon tetrachloride. The combined extracts are shaken with 50 c.c. of a saturated solution of potassium sulphate, the carbon tetrachloride withdrawn, passed through a dry filter, and then oxidized with a solution consisting of 30 c.c. water, 1·5 c.c. H_2SO_4 (specific gravity, 1·84), and 5 grammes of bichromate of potassium, for at least eight hours

in the water-bath. The whole is then distilled in the manner already indicated, first over the naked flame of the Bunsen burner, and then with steam, until in all about 300 c.c. have passed over. The author prefers heating the mixture under a reflux condenser for eight hours, and in the distillation it is better to place a fresh receiver after the carbon tetrachloride has come over. Usually the distilled tetrachloride of carbon shows little or no acidity. The distillate is finally titrated with a decinormal solution of baryta water, first using methyl orange as indicator, and secondly phenolphthalein. The first result gives any free mineral acid (HCl) and the second the valeric acid, which can be calculated into amyl alcohol by multiplying the number of c.c. of decinormal solution of baryta used, and, after the addition of phenolphthalein, by the factor 0·0088. The result may be expressed in terms of iso-butylic alcohol by employing the factor 0·0074.

The colorimetric process for the estimation of higher alcohols employed by French chemists, and notably those of the Paris Municipal Laboratory, is based upon the action of strong sulphuric acid (which produces a more or less yellowish-brown colour, similar to that obtained by adding Nessler reagent to very weak solution of ammonia) upon the higher

alcohols present in alcohol of 50 (in some cases a higher) per cent. strength. The method is admittedly empirical, and cannot be considered as exempt from criticism. It is certainly convenient, and gives fairly constant and comparative results. Sulphuric acid, however, has no action on normal alcohols, and the various iso-alcohols show great differences of sensitiveness to the action of this reagent. This is illustrated in the following table drawn up by M. Mohler, showing the relative degree of coloration given by the higher alcohols (1 in 1,000), in a solution of alcohol of 50 per cent. :

	Per Cent.
Caprylic alcohol - - - -	11
Iso-butylic alcohol - - - -	10
Œnanthylic alcohol - - - -	7
Amylic alcohol - - - -	3

According to MM. Girard and Cuniasse ("Manuel Pratique"), in normal fermentation the higher alcohol which is chiefly present is amylic alcohol, but as iso-butylic alcohol is that which is most sensitive to the sulphuric acid reaction, they choose this alcohol as a standard of comparison for the whole group. As furfural and the aldehydes have an action on sulphuric acid, these are first eliminated in the following way : 50 c.c. of the spirit to be tested are adjusted to 50 per cent. strength, and placed in a flask of a capacity of about 250 c.c. To this quan-

tity are added 3 grammes of chlorohydrate of meta-phenylenediamine or of phosphate of aniline (1 c.c. of phosphoric acid having a density of 1·453, and 1 c.c. of pure aniline oil). Hewitt's reagent (see p. 22) answers this purpose well and most conveniently. A few small pieces of pumice-stone are put in to control the ebullition, the flask is then attached to a reflux condenser, and its contents allowed to boil for one hour, so as to fix the aldehydes. The contents of the flask are then distilled. The distillation is allowed to proceed rapidly over a naked flame, but not so far as to char the residue. The distillate is then brought up to its original volume, and the colorimetric tests applied to it. For developing the colour, 10 c.c. of the distillate are placed in a scrupulously clean flask, and 10 c.c. of monohydrated pure and colourless sulphuric acid are added by means of a pipette. The acid is allowed to trickle slowly from the pipette down the neck of the flask, so that it mixes with the alcohol without developing any marked degree of heat. The flask is next held in a pair of wooden forceps, shaken briskly, and heated over the flame of a Bunsen burner, care being taken to keep the mixture in movement during the heating. As soon as it begins to boil, which will be in about fifteen seconds, it is

set aside to cool. Instead of heating the mixture directly over a flame, it may be heated in a bath of chloride of calcium solution, kept at a temperature of 120° C. As soon as the flask is cold, the contents undergo no further change of colour. The same process is carried out with equal volumes of acid and the standard solution of iso-butylic alcohol (2 per 1,000). The two solutions are matched in the colorimeter, and for this purpose the simple apparatus devised by Hehner is convenient. It consists of two graduated cylinders provided with a draw-off cock near the foot, so that the depths of the two solutions may be brought to show the same intensity of colour. MM. Girard and Cuniasse admit that the test of coloration developed by sulphuric acid is not very delicate, and, in fact, anything below 0·125 gramme of iso-butylic alcohol per litre scarcely shows anything, and consequently an estimation by this method in such a case is hardly possible. M. Saglier, as a means of increasing the action on the higher alcohols, adds a known quantity of furfural to both the standard solution and the spirit to be tested. Thus, in the case of a spirit evidencing a very low amount of higher alcohols there is added before heating, both to the specimen to be tested and the standard which has been selected for com-

parison, 20 drops or more of a solution of furfural (1 in 1,000 in alcohol of 50 per cent. strength). The testing is carried out as described above, without any attention being paid to the addition of the furfural. The colour then produced is intensified, and has a pinkish tint similar to cobalt nitrate. The author finds, however, that its intensity increases with exposure to air.

In order to make the above method more sensitive and more exact, M. X. Rocques proceeds as follows: 100 c.c. of the spirit to be tested, previously distilled and brought to 50 per cent. alcoholic strength, are placed in a small flask of 250 c.c. capacity. Two grammes of chlorohydrate of metaphenylenediamine (to remove aldehydes and furfurol) and a few pieces of pumice are added. The liquid is then boiled gently under a reflux condenser for one hour. It is then cooled and distilled. The distillation, as before, is done quickly, and occupies not more than forty minutes. The distillate is received in a flask graduated exactly to 75 c.c., which will contain the whole of the alcohol, and consequently be of a uniform alcoholic strength of 66·7 per cent. after thorough shaking. With a pipette 10 c.c. of the distillate are measured into the flask of about 100 c.c. measurement, which must be

clean and dry. Then 10 c.c. of monohydrated, colourless sulphuric acid are allowed to trickle down the neck of the flask. The mixture of acid and alcohol is shaken, and then kept at a temperature of 120° C. for one hour. If many flasks are being tested together, it is best to warm them in a calcium chloride bath. The calcium chloride solution is kept at a constant level by the addition of water, which trickles from an inverted flask. The bath is covered with a lid furnished with holes of a diameter slightly bigger than the test flasks. They are kept upright by means of a metal collar which fits round the necks and into the holes in the lid. For each series of tests it is necessary to provide a comparative standard solution which will serve as a colorimetric control. The best solution for the purpose is one of iso-butylic alcohol containing 0·667 gramme of pure iso-butylic alcohol to the litre of alcohol of exactly 66·7 per cent. strength. This solution has the same composition as the product of the distillation of a solution of 0·500 gramme of iso-butylic alcohol in a litre of pure alcohol at 50 per cent. strength would have when the distillation has been carried as far as experience shows to be the best—namely, until the original quantity in the retort is reduced to one-quarter. In this way the comparison between the alcoholic liquid to be tested and the

standard control solution is made under analogous conditions. When the alcoholic liquid to be tested and the standard control solution have each been submitted to the action of the sulphuric acid for the space of one hour at a temperature of 120° C., the flasks are withdrawn from the calcium chloride bath and are set aside to cool. To compare the depth of coloration, M. Rocques employs a Duboscq's colorimeter, but Hehner's colorimeter used in Nessler's test for ammonia in potable waters is applicable, while Mills' colorimeter is excellent for the purpose. The intensity of the colour obtained not being absolutely proportional to the strength of the liquid as regards higher alcohols, the following table giving both the apparent strength obtained by the above formula with the real strength is adopted by M. Rocques for making corrections:

TABLE III.

Apparent Strength.	*Real Strength.*
1·125	1·000
1·009	0·900
0·886	0·800
0·760	0·700
0·640	0·600
0·500	0·500
0·379	0·400
0·255	0·300
0·150	0·200
0·060	0·100
0·019	0·050

According to the experience of MM. Girard and Cuniasse, the coloration obtained by using an alcohol containing less than 0·500 gramme of iso-butylic alcohol per litre is inappreciable, but this limit of 1 in 20,000 is sufficient for all practical purposes. Although it is true that the strengths of 0·5 gramme of iso-butylic alcohol in a litre of 50 per cent. alcohol, and 0·667 gramme of iso-butylic in a litre of 66·7 per cent. alcohol are the same as regards the percentage of higher alcohol per volume of spirit, yet the latter, as obtained by distillation, shows nearly double the sensitiveness to the test than the former. Thus, the solution of 0·667 gramme of iso-butylic alcohol in a litre of alcohol at 66·7 per cent. strength obtained by a three-fourths distillation gives a colorimetric intensity of 100, while a solution of iso-butylic alcohol of 0·500 in a litre of alcohol of 50 per cent. strength only gives a colorimetric intensity of 55, or very nearly half. For this reason the above procedure is adopted. The higher alcohols in ordinary potable spirits are completely expelled on distillation, even when they exist in a high proportion. As a matter of fact, if a solution of iso-butylic alcohol of a strength of 4 grammes to the litre of alcohol at 50 per cent. be taken and distilled, as above directed, the whole of the butylic alcohol will be found in the distillate. This is

in accordance with the author's experience. According to MM. Girard and Cuniasse, this proportion of 800 grammes of higher alcohol per hectolitre of brandy calculated at 100 per cent. strength may be taken to be the maximum which they have ever noted in the many analyses of spirituous liquors which they have made, and therefore the process described above is applicable to any case which may occur in practice. Of course, in the case of a very impure alcohol being met with, it is necessary to dilute it with a known quantity of pure alcohol at 50 per cent. strength before proceeding to distil it. In order to obtain accurate results, the strength should be strictly comparative, for the coloration produced by the sulphuric acid varies, not only with the amount of impurities present, but also with the amount of alcohol present.

The modified method just described gives results sufficiently exact to be utilized in the practical analysis of potable spirits. M. Rocques remarks that in the method of estimation just described the colorimetric standard made use of is a solution of pure iso-butylic alcohol in ethylic alcohol, and that the results are expressed in terms of iso-butylic alcohol. This is the standard adopted by the Paris Municipal Laboratory. It would appear to be more logical to express the results in terms of amylic alcohol, for this

higher alcohol predominates over iso-butylic alcohol in brandy and whisky. Amylic alcohol predominates also in the fusel oil extracted from the first distillation products of potatoes and grain. The results which iso-butylic alcohol and amylic alcohol give under the same conditions have been investigated by MM. Girard and Cuniasse, who carried out their experiments upon fermentation alcohols—that is to say, iso-alcohols obtained by fermentation and scrupulously purified by fractional distillation. Solutions of these alcohols in pure ethylic alcohol at 66·7 per cent. strength were made, and the colorations given when pure sulphuric acid was added and the mixture heated were compared.

With equal quantities of higher alcohols, the coloration produced by amylic alcohol is less than that produced by iso-butylic alcohol. The relation between the two colorimetric intensities is 6 to 10 in the experiments made. If iso-butylic alcohol be taken as a type, it gives for the higher alcohols figures below the truth. Thus, a brandy at 50 per cent. alcoholic strength, containing a mean of 1 gramme of higher alcohols per litre, as expressed in iso-butylic alcohol, contains really more than that amount of amylic alcohol. MM. Girard and Cuniasse, however, think that it would not be de-

sirable to change the standard of comparison hitherto used, for it would create a lamentable confusion in the analytical results of different observers. On the other hand, it is easy to procure a good typical standard solution of iso-butylic alcohol, and the coloration by this higher alcohol is well defined.

The action of strong sulphuric acid is employed by M. Savalle to estimate the *impuretés* of spirit in the following way : 10 c.c. of alcoholic distillate at 50 per cent. strength are placed in a small flat-bottomed flask with a capacity of 125 c.c. ; 10 c.c. of Savalle's reagent—pure monohydrated sulphuric acid—are added. The acid is allowed to trickle down the neck of the flask from a pipette, so that it will mix with the alcohol without much heating. The mixture is then shaken, and heated over the flame of a Bunsen burner. As soon as ebullition commences the flask is removed, covered with a watch-glass, and allowed to cool in a place protected from dust. When cool, the contents of the flask, which are now more or less coloured, are placed in a glass tank having parallel faces each 2·5 centimetres square. The degree of coloration given by the alcohol in this flask is compared with that given by a series of glass slips which can be superposed the one on the other, forming a chromatic scale numbered

from 0 to 15. According to M. Savalle, "0" on his scale represents 1 in 10,000 of impurity. Lovibond's tintometer would appear to be admirably adapted for making this comparison, but so far the author has not tried it. The researches of M. Mohler have shown that the sulphuric acid does not act with the same intensity upon the various by-products which are found in different proportions in alcohol. He submitted a mixture of pure alcohol containing a proportion of 1 in 1,000 of the various *impuretés* noted in the following table, and obtained the results therein given in degrees of the Savalle scale.

TABLE IV.

Alcohols.		*Aldehydes.*		*Ethers.*	
Caprylic	7°	Iso-butylic	9°	Amyl acetate	3°
Iso-butylic	6	Paraldehyde	8	Ethyl acetate	0
Œnanthylic	4	Propionic	9	,, butyrate	0
Amylic	2	Œnanthylic	5	,, Iso-butyrate	0
Propylic	0	Valerianic	5	,, valerianate	0
Iso-propylic	0	Ethylic	3·5	,, caproate	0
Butylic	0	Methylic	2·5	,, œnanthylate	0
Glycerine	0	Acetic	1·5	,, sebate	0
Methylic	0	Butyric	0	,, succinate	0
		Furfural	black	,, benzoate	0
				,, salicylate	0
				,, formate	0
				Methyl salicylate	0

The following table shows that the coloration obtained is not always proportional to the strength of the solution of the *impureté*.

TABLE V.

Nature of Solutions.	*Degrees Savalle for Solutions at* $\frac{1}{1000}$	$\frac{1}{2000}$	$\frac{1}{4000}$
Iso-butylic aldehyde ..	9	3	0·25
Propionic aldehyde ..	7	2·5	0·25
Œnanthylic alcohol ..	4	traces	0
Iso-butylic alcohol ..	6	2·5	0·25
Amyl acetate	3	traces	0

M. Rocques, using solutions of amylic alcohol in ethylic alcohol at 97 per cent. strength, obtained the following results, which, as will be seen, are nearly proportional :

A solution of 1 in 1,000 gave 7
" " 2 " " 13
" " 3 " " 20

The degree of concentration of the alcohol influences the results very markedly, as will be seen in Table VI., owing to the greater or less degree of hydration of the sulphuric acid.

TABLE VI.

Concentration of Alcohol.	*Aldehyde,* $\frac{1}{1000}$.	*Amylic Alcohol,* $\frac{1}{1000}$.
Alcohol at 10 per cent. strength	0·5° Savalle.	0·5° Savalle.
" 50 " "	3·5° "	3·5° "
" 70 " "	9·0° "	9·0° "

It is obvious from this table that to get comparable results the alcohol used must be of nearly the same degree of concentration. The method of heating also affects the results, for sometimes the more volatile impurities evaporate before the heat is sufficiently great to allow of the carbonizing action of the sulphuric acid. MM. Girard and Cuniasse remark that this test is very quickly performed, and is capable of giving an excellent indication of the amount of by-products present in commercial alcohols, while it may be stated that the results given by it accord very correctly with the figures by which the higher alcohols present in a spirituous liquor are estimated. Savalle's test is, of course, empirical, but it is a very useful and expeditious means of roughly differentiating between malt spirit, grape spirit (brandy), and patent spirit, or mixtures of patent spirit. The public analyst will find the following modification by the author of Savalle's test very useful as a preliminary guide as to the quantity of higher alcohols in a spirit, and in his hands it has enabled him to sort quickly all-malt whiskies, genuine brandy, etc., from grain spirit or mixtures of grain spirit.

Ten c.c. of the distillate from a spirit with its alcoholic strength adjusted exactly to 50° C. are

taken. To this are added 10 c.c. of monohydrated sulphuric acid, specific gravity 1·794 (prepared by adding 100 c.c. of pure 1·84 concentrated sulphuric acid to 18 c.c. of water and cooling), in a perfectly clean test-tube 6 inches long by 1 inch wide. The tube is shaken, the act of mixing, which must be completely done, giving rise to development of heat, and a small piece of quill-size glass tubing about ¼ inch long is dropped into the mixture. It is then heated over a naked flame, and a note of the time made. As soon as a few bubbles of steam escape from the fragments of glass tubing, the tube is withdrawn from the flame for twenty seconds, and then returned, and so on. This method is pursued until exactly five minutes have elapsed, when the tube is placed in a stream of cold water. When quite cold, the contents are placed in a small graduated cylinder, and a little alcohol of 50 per cent. strength added to restore the volume of the mixture to 20 c.c. Ten c.c. of a standard solution of iso-butylic alcohol in 50 per cent. alcohol (2 grammes iso-butylic alcohol per litre) are treated in exactly the same way *in the same test-tube*. The solution may then be compared, and the amount of higher alcohols as iso-butylic alcohol calculated. This process gives remarkably consistent results as long as both the standard solution of

iso-butylic alcohol and the distilled spirit are heated in precisely the same way (time intervals, same test-tube) and employed at identical alcoholic strengths. The results, too, approximate to the amount of higher alcohols found by the carbon tetrachloride extraction process. By multiplying the amount of iso-butylic alcohol formed by the factor 1·19 the result may be expressed in terms of amylic alcohol.

CHAPTER VI

THE ESTIMATION OF COMPOUND ETHERS

It is generally assumed that the chief ethereal salt present in brandy and whisky is ethyl acetate, but it is known that other esters occur, amongst which may be mentioned the compounds of caprylic, capric, butyric and caproic acids. On saponifying large quantities of the first runnings of the brandy stills of Cognac the author was able to prepare several ounces of sodium acetate in which very little evidence was obtained of the existence of higher homologues. In carrying out the saponification process in the laboratory, with the view of determining the compound ethers present in spirits, it should be borne in mind that aldehyde and furfural are not without effect upon caustic alkali. Allen (*Journal of the Society of Chemical Industry*, June 30, 1891) finds that the estimation of the ethers from the results of their saponification was liable to be affected by the presence of bodies such as aldehyde

and furfural, which neutralized more or less alkali. Furfural appears to react with a constant ratio of alkali according to the following equation :

$$2C_5H_4O_2 + KOH = KC_5H_3O_3 + C_5H_6O_2.$$

Aldehyde does not appear to give an unvariable factor. Allen has therefore suggested the removal of aldehydes by boiling the spirit under a reflux condenser for two hours with phosphate of aniline —1 c.c. of aniline and 1 c.c. of phosphoric acid, 1·442 specific gravity — before distillation. The author at first adopted this plan, but subsequently, with P. Schidrowitz, found that Hewitt's reagent was more satisfactory, limiting the boiling under a reflux condenser to an hour. In many cases this preliminary treatment may be neglected, for the "real" and "apparent" figures in regard to ether will not differ seriously in the presence of a small proportion of aldehyde and furfural. Nevertheless, it is advisable to prepare sufficient distillate free from aldehydes in the manner indicated, both for the estimation of higher alcohols and the ethers. One hundred c.c. of this distillate is carefully neutralized with decinormal baryta solution using phenolphthalein as indicator. To this neutralized spirit is then added 25 c.c. of an approximately deci-

normal alcoholic solution of soda, and the mixture boiled under the reflux condenser for one hour. After cooling, the excess of alkali is measured by running in decinormal hydrochloric acid until the neutral point is exactly reached. The difference between the number of c.c. of $\frac{N}{10}$ HCl originally required for neutralization by 25 c.c. of the alcoholic soda solution before saponification and the number of c.c. taken to neutralize 25 c.c. after saponification is complete, is an equivalent of the ethers present in the quantity of spirit taken. Each c.c. represents 0·0088 gramme ethyl acetate. It is desirable to carry out a blank experiment with pure spirit, and to make any necessary correction arising from impurities in the reagents, or possibly from the action of the alkali on the glass of the distilling flask. Girard and Cuniasse proceed broadly on the lines described, but they do not appear to adopt special precautions as to the removal of aldehydes and furfural before saponification, while they recommend using exactly 10 c.c. of decinormal potash for the saponification, then adding when it is complete exactly 10 c.c. of decinormal sulphuric acid, and finally titrating for the amount of acid in excess of the alkali added.

CHAPTER VII

ESTIMATION OF FURFURAL

THE estimation of furfural in spirits is of the utmost importance, and fortunately we possess a means of determining this body with tolerable accuracy by a colorimetric process. Furfural characterizes all pot-still spirits ; it is absent in patent spirit, or, if present, it is only in relatively small proportion. Its presence is due to the action of the open fire on the contents of the still during the distillation of the wash, and furfural is, in fact, a product of the action of heat on cellulose and proteids. It occurs in greatest proportion in pot-still whisky ; its amount appears to diminish with age, especially in brandy, old matured brandy containing generally less than immature brandy. The colorimetric process for the estimation of furfural is based upon the fact that it yields with acetate of aniline a fine reddish pink colour. The colour is due to the production of dye-stuffs of a basic character, in which

1 molecule of the aldehyde unites with 2 molecules of the base, $C_4H_3O.CH(C_6H_2Me_2NH_2)_2$. Girard and Cuniasse employ this reaction for the estimation of furfural in spirits in the following manner: 10 c.c. of the alcohol to be tested, previously distilled and brought up to 50 per cent. alcoholic strength, are placed in a graduated tube. In a similar tube are placed 10 c.c. of the standard solution of furfural, of a strength of 0·005 gramme per litre. To each of these tubes is added 10 drops of pure aniline, as colourless as possible, and then to both tubes at once—the time being exactly noted—1 c.c. of acetic acid, pure and free from furfural, is added to each. A quarter of an hour after the acid has been added the two tubes are compared by means of the Duboscq colorimeter. If H be the height of the standard solution of furfural, and "h" the height of the spirit under test, then this latter will contain $0{\cdot}005 \times \frac{H}{h}$ of furfural per litre of alcohol at 50 per cent. The test is satisfactory, but certain precautions must be observed. The aniline oil should be as far as possible colourless, and the acetic acid free from furfural. P. Schidrowitz (*Journal of the Society of Chemical Industry*, June 30, 1902) states that in the case of matured whiskies which he has

examined a yellow colour was developed with the aniline reagent. The writer has not experienced any difficulty of this kind, but it is necessary that the spirit tested should be at exactly 50 per cent. alcoholic strength. Schidrowitz has suggested two methods of overcoming this contingency by, in the first place, using, instead of the ordinary reagent—5 c.c. aniline and 20 c.c. of glacial acetic acid—an acetate solution containing a large excess of aniline. There is then no yellow colour, but the sensitiveness of the reaction is reduced by one-half. The second expedient is to colour the controls. The spirit is first decolourized as far as possible by adding basic acetate of lead, and removing the excess by means of a saturated solution of sulphate of potassium. The reagent is then added to the sample under examination, and to the control, the latter being immediately afterwards coloured with a trace of caramel to match the former. This procedure, it is stated, does not affect the reaction. This process, moreover, overcomes the objection to distillation, during the progress of which furfural might possibly be formed. The author prefers, however, to distil under quite analogous conditions both the control furfural solution and the spirit to be tested. For this purpose the distillation is allowed to

proceed until nine-tenths of the original volume of spirit at 50 per cent. strength are collected. It is important that the reaction should be permitted to proceed for exactly fifteen minutes, and that in all cases the alcoholic strength of the control and the spirit to be tested is the same. Generally speaking, 5 c.c. of the distillate of whisky or brandy made up to 20 c.c. with 50 per cent. alcohol is a convenient quantity to work with, which may be compared in two similar graduated tubes with 5 c.c. of the standard solution of furfural treated in the same way.

Hewitt proceeds as follows for the estimation of furfural (*Journal of the Society of Chemical Industry*, January 31, 1902) : The spirit, if colourless, can be employed directly ; if coloured, then a definite volume is distilled nearly to the last drop, fresh dilute spirit poured into the flask, and the process repeated three or four times. The united distillates are then made up to some definite volume. Two measuring cylinders graduated in c.c., and of the same diameter, are chosen. Into one glass 20 c.c. of the liquid are poured, into the other is measured a quantity of standard furfural solution containing approximately the same amount of furfural solution as is contained in the 20 c.c. of spirit. The volume

of the standard furfural solution is then also made up to 20 c.c. by the dilute spirit. One c.c. of the concentrated aniline acetate solution is added to each vessel, and, after standing ten minutes, the tints, on looking through the spirits against a white background, and also on holding up to the light, are carefully adjusted by addition to one or other vessel of the dilute alcohol. In making up the aniline acetate solution, Hewitt takes equal volumes of freshly-distilled aniline, acetic acid, and water, boils for a few minutes, and cools to the ordinary temperature—any furfural present is thus effectually destroyed .The standard solutions employed are made from freshly-distilled furfural (B. pt. 161° C.), and contain 10, 1, and 0·1 grammes of furfural in 1 litre of alcohol (specific gravity, 0·920).

Hewitt gives the following results in milligrammes per litre of a number of spirits examined in the way indicated :

SCOTCH WHISKIES.

1.	New malt whisky (Glenlivet type) ..	5·5
2.	Whisky of same distillery (five years in cask)	4·4
3.	Foreshots of same distillery.. ..	0·3
4.	Moxed low-wines and feints (same distillery)	0·8
5.	New malt whisky	1·5
6.	„ „	10·5

SCOTCH WHISKIES—*continued.*

7.	New malt whisky	1·6
8.	,, ,, ...	2·0
9.	,, ,, ...	4·1
10.	,, ,, ...	5·5
11.	,, ,, ...	6·3
12.	A mature whole-malt whisky (five years)	4·1
13.	A mature whole-malt whisky (ten years)	3·9
14.	A mature whole-malt whisky (Islay, seventeen years)	3·2

OTHER WHISKIES.

15.	New Irish (1900-1901 ; specific gravity, 0·8513)	6·4
16.	Matured Irish pot-still whisky (? five years)	4·5
17.	Canadian club whisky of 1891 ..	1·5
18.	American rye	1·4

VARIOUS SPIRITS.

19.	Brandy (" Fine Old Cognac ") ..	1·7
20.	Old Jamaica rum	3·2
21.	Dop brandy (Cape Colony)	0·5
22.	,, ,, ,, (another sample)	2·1
23.	Cape Smoke	0·8
24.	Grape brandy (California, 1896) ..	2·2
25.	,, ,, (,, 1898) ..	2·2

The results, it may be noted, are much higher than the amounts of furfural recorded in whisky by MM. Girard and Cuniasse, M. Lusson, P. Schidrowitz, and the author, a fact which may be ascribed

to the method Hewitt adopts of sweeping out the furfural by repeated distillations. It is possible that this method of repeated distillations is open to objection, owing to the probable formation of fresh furfural in the process. By distilling, as previously proposed, both the control and the spirit under examination down to one-tenth of the original volume, distillates are obtained under exactly similar conditions of experiment, and the results are strictly comparable. The author submitted to distillation 100 c.c. of standard furfural—0·01 gramme furfural in 1 litre of 50 per cent. alcohol—until the distillate measured 90 c.c. It was then made up to 100 c.c.; the alcoholic strength was then approximately the same as the original standard. On adding acetic acid and aniline to 5 c.c. of this made up to 20 c.c. with alcohol of 50 per cent. strength, the shade of colour developed after fifteen minutes was exactly the same as that given with 5 c.c. of the undistilled standard solution.

For comparing the tints, Hehner's or Mills' colorimeter may be used, or the simple instrument described in the section on colorimeters.

CHAPTER VIII

THE IMPORTANCE OF TASTE

ALTHOUGH, according to the author's experience, the results of analysis as detailed in the previous chapters will afford data upon which an opinion as to whether or not a spirit is what it is described to be can be based, yet the analyst should go one step further, and cultivate the confirmatory test of taste. He should possess a palate, at any rate, which will enable him broadly to recognise genuine brandy, whisky, and rum. It is obviously a simple matter to make up from a plain spirit an alcoholic fluid of the same alcoholic strength as genuine malt whisky, brandy, or rum, and to add to it artificially-prepared by-products—ethers, acids, aldehydes, higher alcohols, furfural—in such proportion as to make it resemble exactly the chemical composition of a genuine spirit. Such a mixture, while it would be calculated to satisfy the demands of analysis, would be at once rejected by the palate. It is, in fact, not

possible to imitate the æsthetic qualities of genuine spirits by adding by-products to plain spirit, for the simple reason that in potable spirits the aldehydes, acids, ethers, and higher alcohols are of a very complex kind, and it is only for convenience of expression that these are represented in the simplest terms. It is a good plan for the analyst to make up a spirit in this way, which should be kept for purposes of reference in the laboratory, and to that end a matured patent spirit or grain whisky as a spirituous vehicle should be chosen. The grain whisky should be analyzed as to its by-product contents, and then its composition adjusted as regards ethyl acetate, furfural, acetic acid, aldehyde, and amyl alcohol, according as an imitation brandy, whisky, or rum is required for comparison. The sense of smell should similarly be cultivated. The plan of allowing some of the spirit to evaporate on the hands and applying the nose to the residue very often betrays the presence of foreign admixture. The addition of rum to brandy, with a little practice, may easily be detected in this way. Analysis will confirm the diagnosis by disclosing a proportion of ethers inconsistent with other by-products—rum contains an excessive amount of ethers. In applying the sense of taste and smell to whisky, it is best

to dilute the spirit with a little water, which develops the aroma and flavour of an all-malt spirit, while a grain spirit gives little response. Malt whisky after a time curiously develops an opalescence when mixed with water, owing to the separation of probably oily ethers derived from the fats present in the grain. They consist probably of ethylic palmitate and oleate. Blended whisky, on the other hand, keeps more or less bright when water is added to it, according to the amount of genuine malt whisky it contains. Pure patent spirit remains quite clear. It is possible that by carefully measuring the degree of opalescence developed on adding a definite volume of water to whiskies an approximate estimation of the proportions of patent spirit and malt spirit could be made. For the same reason—*i.e.*, that malt whisky contains oily ethers—the spirit, after heating with caustic alkali, froths on distillation, a soap being formed. A good plan of applying the sense of smell to a given spirit is to mix it with some highly-charged soda-water. The gas carries with it the volatile flavourings, the peculiar characters of which a trained nose will readily detect. The difference will be found to be very perceptible between a genuine old malt spirit and patent spirit when tested in this

way. The former has a "fat," somewhat oily smell; the latter gives only a delicate odour, suggesting merely wood or storage in a sherry or plain cask, as the case may be.

Old matured malt spirit or brandy, when mixed with highly-charged soda-water, "creams" on the surface, and the foam is persistent. Patent spirit hardly foams at all; the bubbles break without giving a trace of permanent film on the surface. Very old brandy mixed with soda-water gives in this way a foam as persistent as that of bottled beer, and the smell brought out by the escaping gas is very characteristic and full of ethereal bouquet.

CHAPTER IX

GENERAL CONSIDERATIONS OF THE RESULTS OF ANALYSIS

The French chemists term the by-products of potable spirits the *impuretés*, and the total amount of *impuretés* expressed in milligrammes per 100 c.c. of alcohol present in the spirit—or grammes per hectolitre — gives the *coefficient d'impuretés*. This coefficient varies widely, not only for different spirits, but also for spirits of the same class, according to whether they are young or old. Broadly speaking, however, the relationship of the by-products to each other is preserved, and this relationship is distinctive of a particular spirit. The total amount of secondary products in genuine brandy seldom falls below 300 milligrammes per 100 c.c. of absolute alcohol present in the spirit. The star brandies on the market invariably give figures approximating to that sum—extreme values are 254 and 348. The ratio of ethers to higher alcohols in

brandy of the star type is generally unity. Furfural is also a very constant factor in brandy, the ordinary but genuine kinds giving an average of 2 milligrammes per 100 c.c. of absolute alcohol present in the spirit. In old brandy the acids, ethers, and higher alcohols are decidedly increased, but the furfural is diminished. The total by-products of old brandy may reach the figure of 700 milligrammes per 100 c.c. of absolute spirit.

On the other hand, while average Scotch whisky shows a coefficient of *impuretés* similar to average brandy, the higher alcohols are greatly in excess of the ethers, 3 to 1 being a common ratio, while furfural in whisky always exceeds that found in brandy. This might be expected having regard to the nature of the materials—grapes in the one case and barley malt in the other—from which originally the spirit is derived. Part-malt whisky is readily distinguished from all-malt spirit by a sharp fall in the coefficient of *impuretés*, and in all-grain spirit the by-products are sometimes almost entirely absent. As a rule, however, grain spirit contains some ethers, furfural, and higher alcohols, owing partly to storage in a sherry cask, and partly to incomplete rectification ; but in any case the amount of each is relatively small if existent at all (see Table VII.).

Furfural is rarely present in a grain spirit, and this substance affords some basis for estimating the extent of admixture of plain spirit with a malt whisky or genuine grape-derived brandy. Similarly, the ethers may be taken as the basis of calculation, more particularly in regard to brandy. Plain spirit contains relatively little or no ethers, and its admixture with brandy may therefore be estimated (see examples given in Table XI.).

In genuine rum the ethers are generally in considerable excess of the higher alcohols (see Table X.), and there is no doubt that rum is used to augment the ethers in fictitious brandy (see Table XI.); but the resulting mixture would not contain the relative amounts of by-products present in the genuine article, while rum would add enormously to the volatile acidity. The presence of rum can hardly, however, escape the sense of smell or palate. By far the greater proportion of the whisky sold to the public consists of four-fifths grain spirit, and one-fifth genuine malt spirit, or the proportion of malt spirit may be even less, or there may be no malt spirit present at all.

Typical blends will be found in Table XI., and an approximate idea of the extent of blending may

be gained by comparing the results with those obtained with all-malt whiskies in Table VIII. As, however, grain whisky invariably contains a small proportion of by-products, any calculation based upon these would probably in most cases give an exaggerated estimate of the real proportion of genuine malt spirit.

Genuine brandies show a much less variable composition than malt whisky, according to the results of analyses which are directed to the estimation of the by-products. Brandy, it should be remembered, is sought after for medicinal use on account of its stimulating qualities, which are superior to any other spirit, and this superiority would appear to depend directly upon the invariably and relatively high proportion (and kind) of ethers which it contains, compared with other by-products, and especially the higher alcohols. The proportion of the latter seldom exceeds the proportion of the compound ethers, the ratio of ethers to higher alcohols in genuine brandy very often being exactly as 1 is to 1, while whisky contains three times as much higher alcohols. With genuine rum the reverse is the case—that is to say, the amount of ethers is as much as three times the amount of higher alcohols. According to this, rum should be the most powerful

stimulant we possess, and it is certainly known to be a most vigorous restorative, though often a source of headache. The ethers in rum, however, consist chiefly of ethyl butyrate, which is said to have a less favourable physiological action than ethyl acetate.

The fact that brandy is often trusted by the public for medicinal purposes, and that, as a rule, the genuine article is seldom supplied on draught, an altogether inferior and cheaper spirit—plain spirit, or a mixture of grain spirit flavoured with artificial flavours, to which has been added a little rum or a little genuine brandy—being substituted, is an urgent reason why more control should be exercised over the sale of this spirit.

In a successful prosecution taken under the provisions of the Sale of Food and Drugs Act at Glasgow, the analysts, Dr. Clark and Dr. J. T. Wilson (see Table XI.), based their calculations upon the small proportions of ethers found in the specimens of brandy submitted to analysis. They regarded genuine grape spirit to contain not less than 45 parts of ether in 100,000 parts of proof spirit (78 milligrammes per 100 c.c. of absolute alcohol present in the spirit), whereas the sample analyzed contained only 13·25 parts per 100,000 parts of

proof spirit (23 milligrammes per 100 c.c. of absolute alcohol). The taste and smell of the spirit accorded with the view that featureless spirit had been added. The charge was proven in the Sheriff's view, and his judgment was not altered when the case was brought forward for appeal in the High Court at Edinburgh on December 18, 1903. Several successful convictions obtained elsewhere have been based on similar reasoning.

In regard to brandy, M. Lusson observes that the oxidation products increase in direct ratio to the age of the spirit, but the proportion of the ethers and the higher alcohols varies but slightly. It follows that the relation of the oxidation products to the ethers and the higher alcohols should increase in accordance with the age of the brandy. He is thus led to estimate the age, and therefore the quality, of brandy by what he terms the coefficient of oxidation—that is to say, by the proportion of acids and aldehydes contained in 100 parts of the total by-products. The coefficient of oxidation, he states, is generally between 10 and 36, being 10 for young brandies and 36 for a brandy of forty years old. The figure rises in exact proportion to the age, but shows a constant increase as the age of the spirit increases. According to M. Lusson,

the sum of the ethers and the higher alcohols is always more than 0·300 in Cognac brandy which is free from any admixture with industrial alcohol. It seems to the author that these observations can only apply to brandies of unmixed vintages, and not to blends. Ageing in cask influences the acidity to a certain extent, and not only do the volatile acids increase by slow oxidation, but the spirit dissolves out certain acid principles from the wood which raise the proportion of fixed acids. M. Lusson has made some interesting researches on this matter, and from the results gained he assumes that he can determine the value of a brandy from the point of view of its age.

In regard to the analytical methods employed by MM. Girard and Cuniasse, these chemists state that the results are generally quite definite enough to place an alcohol or a spirituous liquor in the class to which it properly belongs, and it is easy to show whether an alcohol under examination is a genuine spirit or has been adulterated by admixture with trade spirit, and, further, whether an alcoholic liquid has been artificially flavoured, and whether a trade spirit is more or less rectified.

The methods of analysis of alcohols and spirituous liquids adopted by them, and which find a place

amongst others described in these pages, enables them to pronounce definitely, they maintain, as to the nature of the samples. These methods have been practised by them daily in the Municipal Laboratory, Paris, for more than ten years, and they have always afforded singularly consistent results. Moreover, these results have been verified by different observers, and their conclusions have proved the same.

Finally, the author has been enabled by the methods of analysis described in the text to deduce approximately the amount of admixture in various spirits, and especially whisky and brandy, submitted to him by well-known distillers, who knew accurately how they were made up, and in every instance the deduction was very fairly correct. Moreover, when the analytical indications were adjudged to be in favour of a spirit being genuine and unmixed, the conclusion invariably proved to be in accordance with fact.

CHAPTER X

COLORIMETERS

The colorimeter employed by MM. Girard and Cuniasse is one devised by Duboscq, which is not readily obtainable in this country. The two solutions are viewed through a disc, one half of which receives the light from the standard, and the other half from the spirit under examination. The adjustment is very accurate.

A useful colorimeter for the analysis of spirits is that devised by Mills. It consists of a glass jar closed at the top by a cap. The cap is perforated in the middle, and carries a short tube in which slides a bent glass rod, and supporting exactly at right angles to the axis of the jar a flat circular opaque white disc. In the bottom of the jar are laid a red and green glass disc, one above the other, which form a black background to the white disc. The white disc is lowered to the bottom of the jar by moving its rod, and the jar is filled exactly to

so many divisions with the standard liquid. The white disc is raised until on looking vertically down through the liquid at the disc the depth of tint appears suitable. A second apparatus is then filled to the same number of divisions with the liquid to be tested, and its disc is adjusted until the colours of the columns of the liquid in the two jars appear of equal intensity. The lengths of these columns are noted, and the comparison is repeated, using preferably a different length of column of the standard.

The relative strength of the solutions varies inversely as the lengths of the columns, so that if 1 c.c. of the standard solution correspond with 10 parts by weight of the substance estimated, the weight of that substance in 1 c.c. of the test solution will be

$$\frac{\textit{length of column of standard solution multiplied by } x}{\textit{length of column of test solution}}$$

The Nesslerizing tubes adopted by Hehner are still more convenient and easy of application in the case of the colorimetric analysis of spirits, but they should be of smaller capacity and calibre than those used in the estimation of ammonia in waters, while the draw-off cock should be near the bottom of the cylinder. The two cylinders are placed side by side on white paper, and to one of them is added the

spirit to which the reagent has been added. To the other tube a suitable and known amount of standard is added. The two liquids are looked at vertically, and the darker is allowed to slowly run off into a clean beaker until their colours are equal. The comparison may be repeated after filling up from the beaker. The mode of calculation is the same as in former cases.

The author has been accustomed to employ two graduated tubes about 1 inch in diameter. At the lower end is fitted a rubber cork, through the perforation of which passes a glass rod, terminating in an opal disc nearly fitting the tube. The discs may be pushed up or down until the colours are equal. The calculation is the same as before.



APPENDIX.

TABLE VII.—TYPES OF GRAIN AND ROOT SPIRITS.

Description of Spirit.	*Volatile Acidity as Acetic Acid.*	*Aldehydes.*	*Furfural.*	*Ethers as Ethyl Acetate.*	*Higher Alcohols.*	*Total Secondary Products.*	*Observer.*	*Remarks.*
Grain spirit (French) ..	2·5	0·1	nil	3·60	2·90	9·10	Girard and Cuniasse	Pure spirit
Grain spirit (French) ..	2·50	nil	nil	3·60	5·70	11·80	Do.	Pure spirit
Grain spirit (Nord) ..	5·00	nil	nil	3·60	nil	8·60	Do.	Pure spirit
Grain spirit (new, supplied to London)	8·40	4·90	0·35	23·80	traces	37·45	Vasey	Typical grain spirit
Grain spirit (supplied to London, five years old)	20·40	5·30	0·21	11·73	48·62	86·26	,,	Stored in plain cask
Grain spirit (supplied to London, nine years old)	nil	17·50	nil	49·64	nil	67·14	,,	Grain spirit stored in sherry casks
Grain spirit (supplied to London, nine years old)	61·20	11·22	0·23	32·65	85·00	190·30	,,	Grain whisky stored in sherry casks
Grain spirit (new) ..	nil	3·70	nil	47·60	67·70	119·00	Schidrowitz	——
Grain spirit (new) ..	nil	5·90	nil	56·20	84·90	147·90	,,	——
Grain spirit (five years old)	13·50	9·10	nil	72·40	77·40	172·40	,,	——
Beetroot spirit	5·00	11·50	nil	18·60	7·30	42·40	Girard and Cuniasse	Badly rectified
Beetroot spirit	2·50	nil	nil	3·60	2·50	8·60	Do.	Highly rectified

TABLE VIII.—TYPES OF GENUINE WHISKIES.

Description of Spirit.	*Volatile Acidity as Acetic Acid.*	*Aldehydes.*	*Furfural.*	*Ethers as Ethyl Acetate.*	*Higher Alcohols.*	*Total Secondary Products.*	*Observer.*	*Remarks.*
New Whisky :								
Scotch, first runnings ..	36·00	62·50	1·20	129·94	200·00	429·64	Vasey	——
,, distillate half run	48·00	6·50	1·40	36·60	160·00	252·50	,,	——
,, at striking still ..	36·00	2·00	2·00	21·96	120·00	181·96	,,	——
,, running at proof	48·00	1·50	3·22	5·48	trace	58·30	,,	——
Old Highland whisky : Eight years old	48·00	14·20	4·00	89·68	200·00	355·88	,,	Genuine all-malt whisky
Twenty-five years old ..	64·80	66·06	5·40	125·13	180·00	441·39	,,	Genuine old matured
Scotch whisky : New ..	25·40	11·40	6·20	61·90	199·40	304·30	Schidrowitz	——
New	14·30	3·00	3·40	90·00	263·30	574·00	,,	——
Four years old	61·10	35·20	2·80	111·00	160·80	370·90	,,	Stored in sherry cask
Five years old	20·10	21·30	3·70	109·40	148·30	302·80	,,	Stored in plain cask
(Age not given)	48·00	26·60	4·00	66·80	240·00	385·40	Girard and Cuniasse	——
Six years old	51·90	32·50	4·00	79·30	276·00	443·70	Do.	——
Nine years old	65·40	28·00	3·90	75·60	239·70	412·60	Do.	——
Liqueur, very old ..	67·20	30·00	4·00	77·40	264·00	442·60	Do.	——
Irish whisky : New ..	20·88	6·52	0·43	7·65	174·00	209·48	Vasey	Genuine whisky but ethers abnormally low
Seven years old	41·76	11·22	3·40	20·91	204·00	281·29	,,	Genuine malt
Eight years old	51·60	27·90	3·60	51·60	327·20	461·90	Girard and Vasey	——
Ten years old	51·90	14·41	3·46	30·44	259·50	359·71	Cuniasse	Well-matured Irish whisky
Very old special	38·20	30·80	3·90	52·50	351·90	477·30	Girard and Cuniasse	——

TABLE IX.—TYPES OF BRANDIES.

Description of Spirit.	*Volatile Acidity as Acetic Acid.*	*Alde-hydes.*	*Fur-fural.*	*Ethers as Ethyl Acetate.*	*Higher Alcohols.*	*Total Second-ary Pro-ducts.*	*Observer.*	*Remarks.*
Brandy:								
Grande champagne, 1811	300·16	47·37	0·80	193·29	371·52	913·14	The *Lancet* Commission on Brandy, November, 29, 1904	
,, ,, 1875	165·19	21·22	0·95	144·64	173·92	505·82		
,, ,, 1893	68·96	7·27	1·97	162·96	124·16	365·32		
Petite champagne, 1895	72·96	9·74	2·33	124·72	162·13	371·88		
Bois, 1895	70·21	12·92	1·56	113·35	144·83	342·87		
Three star	77·32	12·60	1·70	110·00	120·58	232·20		
Two star	65·70	12·16	2·63	103·43	108·45	292·37		
One star	65·02	10·03	2·36	97·13	80·28	254·82		
Very old liqueur ..	152·71	42·42	1·69	182·83	258·76	634·41		
1817	394·00	36·00	3·10	128·70	112·50	1174·30	M. Lusson	From the Bois district
1860	202·10	48·10	1·20	133·30	345·40	730·10	Girard and Cuniasse	——
1875	114·00	28·90	1·00	143·30	173·60	460·80	Do.	——
1896	229·00	11·50	1·20	101·30	260·00	403·00	Do.	From Gemozac district
Champagne, 1852 ..	343·70	42·40	2·80	169·70	405·00	963·60	M. Lusson	Genuine old Cognac brandy

TABLE X.—TYPES OF RUM AND GIN.

Description of Spirit.	*Volatile Acidity as Acetic Acid.*	*Aldehydes.*	*Furfural.*	*Ethers as Ethyl Acetate.*	*Higher Alcohols.*	*Total Secondary Products.*	*Observer.*	*Remarks.*
Jamaica rum ..	28·00	8·40	2·80	399·00	90·60	528·80	Vasey	Genuine Jamaica rum
,, ,, ..	176·00	22·10	2·90	443·10	93·90	738·00	Girard and Cuniasse	——
Gin, unsweetened ..	nil	1·78	nil	37·28	44·60	83·66	Vasey	——
Gin, Nord	40·40	9·90	0·30	18·50	27·90	97·00	Girard and Cuniasse	——

TABLE XI.—TYPES OF BLENDED SPIRITS.

Description of Spirit.	*Volatile Acidity as Acetic Acid.*	*Alde-hydes.*	*Fur-fural.*	*Ethers as Ethyl Acetate.*	*Higher Alcohols.*	*Total Second-ary Pro-ducts.*	*Observer.*	*Remarks.*
Public-house brandy	79·41	7·35	0·61	32·35	49·02	168·74	The *Lancet* Commission on Brandy, November 29, 1903	Flavoured grain spirit
,, ,, ,,	150·61	6·60	0·44	71·69	58·70	288·04		Grain spirit mixed with some rum
Railway Restaurant	91·62	5·93	0·74	80·17	113·11	291·30		Brandy blended with plain spirit
Brandy, one star ..	29·50	16·80	1·00	86·50	115·50	249·30	Girard and Cuniasse	Brandy and plain spirit
,, two star ..	29·60	23·30	1·00	68·90	96·00	218·80	Do.	Brandy and plain spirit
Fine champagne ..	97·00	23·40	1·40	74·80	91·00	226·30	Do.	Brandy and plain spirit
Brandy	33·60	2·18	0·70	26·25	—	—	Dr. Clark and Dr. J. T. Wilson	50% foreign spirit
,, ...	46·20	2·62	0·70	26·25	—	—	Do.	50% ,, ,,
,, ...	49·25	4·37	0·61	21·56	—	—	Do.	65% ,, ,,
,, ...	33·60	13·12	1·05	43·12	—	—	Do.	35% ,, ,,
,, ...	29·40	3·50	0·78	15·48	—	—	Do.	62% ,, ,,
,, ...	86·80	18·65	2·90	47·17	—	—	Do.	37% ,, ,,
,, ...	49·25	17·50	2·20	56·17	—	—	Do.	28% ,, ,,
,, ...	54·00	17·50	1·69	44·80	—	—	Do.	43% ,, ,,
,, ...	98·17	10·67	1·62	61·65	—	—	Do.	20% ,, ,,

TABLE XI.—TYPES OF BLENDED SPIRITS—*continued.*

Description of Spirit.	*Volatile Acidity as Acetic Acid.*	*Aldehydes.*	*Furfural.*	*Ethers as Ethyl Acetate.*	*Higher Alcohols.*	*Total Secondary Products.*	*Observer.*	*Remarks.*
Scotch whisky ..	12·30	10·25	0·51	5·33	102·50	130·89	Vasey	Grain whisky matured in sherry cask
,, ,, ..	39·06	14·32	3·49	106·76	108·50	272·13	,,	Blended malt spirit
,, ,, ..	15·56	10·65	2·55	72·03	85·20	185·99	,,	Blended with grain spirit
Public-house Scotch whisky	16·80	10·00	nil	8·23	nil	35·03	,,	Grain spirit (probably foreign)
Liqueur whisky ..	12·00	20·00	2·50	70·40	180·00	284·90	,,	Blended whisky
Whisky obtained in Paris	11·90	15·30	2·20	39·40	131·40	200·20	Girard and Cuniasse	Blended malt and grain
Whisky	trace	7·50	nil	106·50	93·80	277·80	*British Medical Journal*	Molasses patent spirit, part molasses, part maize
,, ...	trace	4·30	nil	105·00	166·60	275·90	Do.	——
Rum	122·40	6·00	1·30	71·80	18·10	289·60	Girard and Cuniasse	Rum plus grain spirit
,, ...	93·00	19·60	1·00	92·60	31·90	238·10	Do.	Rum plus grain spirit

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